

Dehydrogenation of Coal by Metal Salt Catalysts

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INTRODUCTION

Coal is dehydrogenated below 400°C by a number of catalysts. Mazumdar et al¹⁻⁴ obtained up to 50% removal of hydrogen with sulfur, iodine and benzoquinone as catalysts. Reggel et al⁵⁻⁷ used palladium catalyst supported on CaCO₃ and phenanthridine solvent to dehydrogenate coals. The hydrogen is reported to originate primarily from the hydroaromatic portions of the coal. Mazumdar et al⁸ reported on the pyrolysis at 600°C of coal dehydrogenated by sulfur. The coals show an increased yield of char and a corresponding decrease in tar yields. Untreated coals show a dependence of tar yield on the fraction of hydroaromatic structures in the coals. The decreased tar yields in dehydrogenated coals was attributed to the destruction of hydroaromatic units during dehydrogenation. Other processes are probably involved, although the hydroaromatic groups may be the major source of hydrogen.

Zinc halides and stannous chloride are known to be effective coal hydrogenation catalysts⁹. Their capacity to rapidly hydrogenate coal has stimulated the study of the mechanism of catalytic hydrogenation and of the properties of coal impregnated with metal salts. A previous report¹⁰ presented some pyrolysis results. Coals impregnated with zinc halides and stannous chloride were found to yield less hydrocarbon gases and tar during low-temperature pyrolysis. The possibility that the suppression of tar evolution was caused by destruction of hydroaromatic groups lead to the present study of the dehydrogenation of coal by zinc chloride.

EXPERIMENTAL

Hiawatha, Utah coal was impregnated with zinc chloride as previously described¹⁰. The analysis of Hiawatha coal is shown in Table I.

Table I. Analysis of Hiawatha Coal

% Ash	4.1	% C	79.5
% V. M.	43.1	% H	5.2
% F. C.	52.8	% N	1.6
Heating value	14,100 Btu/lb.	% S	0.6
		% O	13.4
		% O (difference)	13.1

Six gram samples were heated at 5°C/min under a nitrogen flow. Evolved gases were sampled at 50°C intervals and analyzed by gas chromatography. Hydrogen was determined using argon carrier gas, a molecular sieve column and a thermal conductivity detector operating at 25°C and low bridge currents. Hydrocarbon gases were removed prior to analysis with a liquid nitrogen trap. This method does not give quantitative yields of hydrogen but only relative yields.

Coal and impregnated coal samples were dehydrogenated by palladium after the method of Reggel et al⁵⁻⁷. One quarter gram of coal, 0.3 grams of catalyst (1% Pd) and 3.5 grams of phenanthridine were refluxed at 345°C for 12 hours. The

volume of evolved gas was measured and the gases analyzed to determine the yield of hydrogen.

RESULTS AND DISCUSSION

The weight loss and hydrogen evolution during pyrolysis of coal and coal impregnated with 12% by weight ZnCl_2 are shown in Figure 1. The coal shows hydrogen evolution occurring above 300°C , with a maximum at about 600°C . In the presence of ZnCl_2 , the initial hydrogen evolution is shifted to 200°C and two maxima appear. Significant amounts of molecular hydrogen are evolved below 400°C while the evolution of hydrogen at higher temperatures is unaffected. The impregnated coal also shows a decrease in weight loss above 400°C compared to the unimpregnated coal.

Results from the catalytic dehydrogenation with Pd are shown in Table II.

Table II. Dehydrogenation with Palladium Catalyst

Sample	H_2 evolved ml/gm-coal at STP	% H_2 evolved
Hiawatha coal	311	44.0
12% ZnCl_2 /H coal	356	50.4
12% ZnCl_2 /H coal (without Pd catalyst)	243	34.4
200°C Residue from pyrolysis of 12% ZnCl_2 /H coal	353	50.0
400°C Residue from pyrolysis of H coal	140	--
400°C Residue from pyrolysis of 12% ZnCl_2 /coal	281	--

Hiawatha coal shows dehydrogenation to the extent of 311 cc/g, corresponding to 44.0% of the original hydrogen. When impregnated with 12% ZnCl_2 , the coal shows additional dehydrogenation, while the impregnated coal shows significant dehydrogenation under the experimental conditions without Pd present. An impregnated coal heated to 200°C and then cooled prior to dehydrogenation shows no difference from an unheated sample. This is to be expected since pyrolysis results show no affect below 200°C . An impregnated coal heated to 400°C prior to dehydrogenation shows less hydrogen evolution than an unheated sample, but significantly more than an unimpregnated coal heated under the same conditions.

Palladium is thought to be a specific catalyst for the dehydration of hydroaromatic groups. The hydroaromatic groups in coal are evolved as tar or otherwise destroyed during the early stages of pyrolysis. The coal sample heated to 400°C shows only about 45% as much hydrogen available for removal by Pd as compared to an unheated coal. When hydroaromatic structures in coal are removed prior to heating, the yield of tar is decreased. These experiments indicate that ZnCl_2 has the property of dehydrogenating coal below 400°C . The catalytic dehydrogenation experiments with Pd indicate that some of the hydrogen comes from hydroaromatic groups in the coal. An impregnated sample heated to 400°C is altered in such a way that tar yields at temperatures above 400°C are reduced, but the sample still contains nearly all the hydrogen that can be removed with Pd catalyst. The same behavior on pyrolysis is noted with coals impregnated with ZnBr_2 , ZnI_2 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, all of which show catalytic hydrogenation ability. A comparison of

metal chlorides and metal sulfates, indicates little dehydrogenation activity by the sulfates although some sulfates are reported to be good coal hydrogenation catalysts in longer-residence-time reactors.

The mechanism of catalytic dehydrogenation of coal by ZnCl_2 is not clear. The mechanism is different than in the case of dehydrogenation with sulfur since molecular hydrogen is produced. No solvent is required for dehydrogenation with ZnCl_2 . Zinc chloride is altered when impregnated on coal surfaces and heated. The nature of the compound formed between coal and ZnCl_2 and the mechanism of reaction are being studied.

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FIGURE 1. WEIGHT LOSS AND HYDROGEN EVOLUTION DURING PYROLYSIS OF
HIAWATHA COAL AND HIAWATHA COAL IMPREGNATED WITH 12% ZnCl_2 .

